METHOD FOR THE DETERMINATION

OF AIR-PHASE PETROLEUM HYDROCARBONS (APH)

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Massachusetts Department of Environmental Protection

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METHOD FOR THE DETERMINATION OF AIR-PHASE PETROLEUM HYDROCARBONS

MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

1.0 SCOPE & APPLICATION

1.1 This method is designed to measure the gaseous-phase concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in air and soil gas. Volatile aliphatic hydrocarbons are collectively quantitated within two carbon number ranges: C_5 through C_8, and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 28°C and 245°C.

1.2 This method is based on the collection of whole air samples in SUMMA® passivated stainless steel canisters, with subsequent analysis by gas chromatography/mass spectrometry (GC/MS). This method should be used by, or under the supervision of, analysts experienced in the use of GC/MS instrumentation.

1.3 This method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994). It is intended to generate data in a format suitable for evaluation by that approach, and generate data that may be used in the characterization of risk at sites undergoing evaluation under the Massachusetts Contingency Plan (310 CMR 40.0000).

1.4 This method is also able to measure the individual concentrations of the Target APH Analytes 1,3-butadiene, methyl-tert-butylether (MtBE), benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and 2-methylnaphthalene in air and soil gas.

1.5 Petroleum products suitable for evaluation by this method include gasoline, as well as the volatile fractions of mineral spirits, kerosene, #2/diesel fuel oil, jet fuels, and certain petroleum naphthas. This method is not designed to measure the particulate-phase concentrations of heavier molecular weight hydrocarbon compounds.

1.6 The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic fractional ranges is approximately 25 - 100 $\mu g/m^3$. The RL of this method for the Target APH Analytes is compound-specific, and ranges from approximately 2 to 20 $\mu g/m^3$.

1.7 This method includes a series of data manipulation steps to determine the concentrations of aliphatic and aromatic ranges of interest. These steps may be taken by the laboratory or by the data user.

1.8 Data generated using this method must be reported using the form/format provided.

1.9 This is a performance-based method. Modifications to this method are permissible, provided that adequate documentation exists, or has been developed, to demonstrate an equivalent or superior level of performance. MADEP encourages methodological innovations which (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes. Laboratories that modify this method must achieve all required performance and acceptance standards, and must have on file a Standard Operating Procedure which thoroughly describes the revised or alternative method, and documentation which demonstrates an equivalent or superior level of performance. All significant modifications to the method must be disclosed and described on the data report form, as detailed in Section 11.0.

1.10 Additional information on the MADEP approach to characterizing the risks posed by petroleum hydrocarbons may be obtained from http://www.magnet.state.ma.us/dep/bwsc/vph_eph.htm

2.0 SUMMARY OF METHOD AND DATA QUALITY OBJECTIVES

2.1 Samples are collected in precleaned, evacuated SUMMA® passivated stainless steel canisters.

2.2 A specified volume of sample is withdrawn from the canister through a mass flow controller using a vacuum pump. The sample is cryogenically concentrated to a volume of less than one mL in a nickel trap filled with nonsilanized glass beads. If samples are known to contain high humidity, a Nafion® dryer may be used prior to the nickel trap. The Nafion® dryer will remove excess moisture in the sample, but may also remove some of the more polar compounds (including MtBE). Concentrators with alternative water management techniques are available, and should be used if necessary.

2.3 Following preconcentration, the sample is transferred and refocused onto the inlet of a capillary column on a gas chromatograph using a cryofocusing accessory. This step further concentrates the sample to increase sensitivity.

2.4 The sample is then injected into a gas chromatograph, which is used to separate the individual compounds and hydrocarbon fractions of interest. All compounds are detected using a mass spectrometer. Target APH Analytes are identified and quantitated using characteristic ions. Collective concentrations of C_9-C_{10} Aromatic Hydrocarbons are quantitated using extracted ions. Collective concentrations of aliphatic hydrocarbon fractions are quantitated using a total ion chromatogram, subtracting out Target APH Analytes and C_9-C_{10} Aromatic Hydrocarbons.

2.5 This method is based on USEPA Method TO-14, *Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA® Passivated Canister Sampling and Gas Chromatography (GC) Analysis.*

2.6 Data Quality Objectives should be developed and applied for sampling and analytical efforts involving the use of this method. Key parameters of interest include (a) the need for and extent of time-integrated air samples, (b) the acceptability of Reporting Limits achievable by the laboratory for the samples of interest, and (c) identification and reporting of target and non-target analytes.

3.0 DEFINITIONS AND UNITS OF MEASURE

3.1 Definitions

3.1.1 **Absolute canister pressure** is defined as Pg + Pa, where Pg = gauge pressure in the canister (psig) and Pa = barometric pressure.

3.1.2 **Absolute pressure** is defined as the pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPA, mm Hg, or psia.

3.1.3 **Air-Phase Petroleum Hydrocarbons (APH)** are defined as collective fractions of hydrocarbon compounds eluting from isopentane to 1-methylnaphthalene, excluding Target APH Analytes. APH is comprised of C_5 -C_8 Aliphatic Hydrocarbons, C_9-C_{12} Aliphatic Hydrocarbons, and C_9-C_{10} Aromatic Hydrocarbons.

3.1.4 **APH Calibration Check Standard** is defined as a gaseous-phase mixture of APH Component Standards that is used to periodically check the calibration state of the

GC/MS system. The APH Calibration Check Standard is prepared from the same stock solution as the APH working/calibration standards, and is generally one of the mid-level gaseous dilutions.

3.1.5 **APH Component Standard** is defined as a 30-component mixture of the aliphatic and aromatic compounds listed in Table 1. The compounds comprising the APH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Target APH Analytes, (b) define and establish the retention time windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average chromatographic response factors that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.1.6 **APH Working Standards** are defined as a series of gaseous-phase mixtures prepared and/or contained in SUMMA® passivated stainless steel canisters. Working Standards are prepared by injecting methanol-based dilutions of the APH Component Standard into humidified canisters, or may be purchased as certified mixtures. Different volumes of the APH Working Standards are used to create multi-level gaseous-phase calibration standards.

3.1.7 **C_5 through C_8 Aliphatic Hydrocarbon**s are defined as all aliphatic hydrocarbon compounds which elute from isopentane to just before n-nonane (C_9).

3.1.8 **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which elute from n-nonane to just after 1-methylnaphthalene.

3.1.9 **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds which elute from just after o-xylene to just after 1-methylnaphthalene, excluding naphthalene and 2-methylnaphthalene, which are quantitated and evaluated separately as Target APH Analytes.

3.1.10 **Cryogen** is defined as the refrigerant used to obtain very low temperatures in the cryogenic trap of an analytical system. A typical cryogen is liquid nitrogen (boiling point = -196°C).

3.1.11 **Gauge pressure** is defined as the pressure measured above atmospheric pressure (as opposed to absolute pressure). Zero gauge (0 psig) is equal to ambient atmospheric (barometric) pressure.

3.1.12 **Humidified Canister** is defined as a SUMMA® passivated stainless steel canister fortified with HPLC-grade water to simulate moisture conditions in real-world samples. For a 6-liter SUMMA® canister pressurized to 30 psig, a humidified canister is defined to contain 130 µL of HPLC-grade water. This is equivalent to a relative humidity of 32% at 25°C.

3.1.13 **Laboratory Control Spike** is defined as a Humidified Canister fortified with a gaseous-phase mixture of the APH Component Standard obtained from a different stock solution than the APH working/calibration standards.

Table 1. APH Component Standard

Compound	CAS Number	Target APH Analyte	APH Range Marker	Retention Time (minutes)[1]	MDL[2] (µg/m^3)	MDL[2] ppbV	Mol Wt. g/mol
1,3-Butadiene	106990	✓		5.94	2.8	1.2	54.09
Isopentane	78784		✓	8.63			
Methyl-tert-butylether	1634044	✓		14.57	44	12	88.15
n-Hexane	110543			16.46			
Benzene	71432	✓		20.14	2.2	0.69	78.11
Cyclohexane	110827			20.72			
2,3-Dimethylpentane	565593			21.54			
n-Heptane	142825			23.82			
Toluene	108883	✓		27.83	1.9	0.49	92.14
n-Octane	111659			30.85			
Ethylbenzene	100414	✓		34.24	2.3	0.52	106.17
2,3-Dimethylheptane	3074713			34.66			
m-Xylene	108383	✓		34.85	4.9	1.1	106.17
p-Xylene	106423	✓		34.85	4.9	1.1	106.17
o-Xylene	95476	✓	✓	36.27	2.4	0.55	106.17
n-Nonane	111842		✓	37.33			
Isopropylbenzene	98828			38.31			
1-Methyl-3-ethylbenzene	620144			40.56			
1,3,5-Trimethylbenzene	526738			41.02			
n-Decane	124185			43.32			
1,2,3-Trimethylbenzene	526738			44.20			
p-Isopropyltoluene	99876			44.34			
Indene	95136			45.30			
Butylcyclohexane	1678939			45.34			
n-Undecane	1120214			48.76			
Naphthalene	91203	✓		51.69	9.5	1.8	128.17
n-Dodecane	112403			52.29			
Hexylcyclohexane	4292755			53.52			
2-Methylnaphthalene	91576	✓		54.84	9.3	1.6	142.20
1-Methylnaphthalene	90120		✓	55.32			

[1]Results obtained using an RTX-1 column and chromatographic conditions described in Sections 6.7 and 9.2, respectively

[2]Single laboratory MDL study; see Appendix 1 for more details

3.1.14 **Laboratory Method Blank** is defined as a Humidified SUMMA® Canister pressurized with zero air.

3.1.15 **Target APH Analytes** are defined as 1,3-butadiene, methyl-tert-butylether (MtBE), benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and 2-methylnaphthalene.

3.2 **Units of Measure**

The units of measure referenced in this method for volume, concentration, and pressure are reflective of the conventions and standards that are commonly used by practitioners within this field, and/or the conventions and standards associated with commonly available instrumentation and equipment. While the volume of liquids are always expressed in µL or mL, the volume of gases are expressed in cubic centimeters (cc or cm^3), mL, and/or L. While the concentration of liquid solutions are always expressed in µg/mL, the concentration of gaseous mixtures are expressed in µg/mL, ng/L, $\mu g/m^3$, ppbV and/or ppmV. Units of pressure measurement are expressed in terms of psig, psia, torrs, millitorrs, inches of Hg, and/or mm of Hg. Confusion in this regard may be further compounded given that liquid (methanol-based) stock and primary dilution standards are used to generate gaseous-phase APH working and calibration standards**. For these reasons, adequate care must be exercised to understand the context and meaning of measurement units used and referenced throughout this document.**

4.0 INTERFERENCES AND METHOD LIMITATIONS

4.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

4.2 Polar compounds such as methyl-tert-butylether will exhibit decreased recovery and sensitivity when the Nafion® dryer is used in the sample preconcentration step. This may be a significant problem for highly humid samples, including soil gas samples.

4.3 System carryover can be a potential problem, particularly for the heavier molecular weight hydrocarbons such as naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. Carryover can occur after the analysis of standards or high concentration samples. Measures which must be taken to remove this contamination can include the analysis of multiple blanks, the use of humidified air through the system, and occasional bakeout or replacement of the Nafion® dryer. It should be noted that background levels of these compounds may still be present even after these measures have been taken.

4.4 If the Nafion® dryer is not utilized during the sample preconcentration step to remove moisture, the chromatography of the beginning of the analysis (up to approximately 20 minutes) may be compromised. This would affect the first internal standard and compounds up through C_6. Although the peak shapes of these compounds may not be ideal, reproducibility and accuracy for these compounds have been found to be acceptable up to approximately 33% relative humidity.

4.5 High methane levels and/or carbon dioxide levels may also interfere with the chromatography in a similar manner as described above for moisture. Dilutions may be performed on these samples; however, the Reporting Limits will then be raised.

4.6 Certain organic compounds not associated with the release of petroleum products, including chlorinated solvents, ketones, and ethers will be detected by this method and quantified within an aliphatic or aromatic hydrocarbon range. **When noted by the analyst, the identification and/or**

quantitation of such compounds must be disclosed on the laboratory reporting form or supporting documentation. If necessary and/or desirable, additional sample cleanup steps and/or analytical procedures may be employed to minimize or further document the presence of such compounds.

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 Microliter syringes – 10, 25, 50, 250, and 500 μL.

6.2 2.0 mL volumetric flasks with ground glass stoppers, Class A.

6.3 Pasteur pipettes.

6.4 2.0 mL amber vials with 8-mm septa (red PTFE/Silicone) and polypropylene screw caps.

6.5 Six (6) liter SUMMA® passivated stainless steel canisters or equivalent (e.g., silica lined canisters).

6.6 Canister sample concentrator:

6.6.1 The concentrator system consists of three separate pieces of equipment: (1) Graseby Nutech Model 3600 (or equivalent) VOC autosampler, (2) Graseby Nutech Model 3550A (or equivalent) cryogenic concentrator using liquid nitrogen with Nafion® dryer option, and (3) Graseby Nutech Model 354A (or equivalent) cryofocusing accessory.

6.6.2 A vacuum pump delivers the sample from the autosampler to the cryogenic concentrator via stainless steel tubing.

6.7 Gas Chromatograph System

6.7.1 An analytical system complete with a temperature programmable gas chromatograph for use with a capillary column is required.

6.7.2 The required chromatographic column is: RTX-1; 60 meters, 0.25 mmID, 1-micron film thickness, or column with equivalent chromatographic properties.

NOTE: Based upon data obtained from the MADEP VPH Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantitation of aliphatic and aromatic compounds within the fractional ranges specified in this method. Substitution of the required column is not allowed, unless it can be demonstrated that the selected column has equivalent chromatographic properties and retention times for the aliphatic and aromatic compounds and ranges of interest.

To demonstrate equivalency of column chromatography, a neat gaseous gasoline standard must be analyzed on both the required column and the proposed substitute column, with all other run and system parameters held constant. The concentrations of C_5 - C_8 and C_9 - C_{12} Aliphatic Hydrocarbons must be determined for each column. The Relative Percent Difference between the concentrations of each fraction obtained for each column must be equal to or less than 25%.

6.7.3 A transfer line is required from the cryofocusing assembly to the chromatographic column, consisting of a deactivated 0.32-mm capillary tubing connected to the column with a Restek Vu-Union (or equivalent) connector.

6.8 Mass Spectrometer System

6.8.1 The mass spectrometer must be capable of scanning from 35 to 250 amu every 3 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 2 when 10 ng of 4-bromofluorobenzene is injected.

Table 2. BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0 – 40.0 percent of the base peak
75	30.0 – 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 – 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 – 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 – 9.0 percent of mass 176

6.8.2 A data station is required that is capable of storing and reintegrating chromatographic data and capable of determining peak areas using a forced baseline projection.

7.0 REAGENTS AND STANDARDS

Liquid Stock and Primary Dilution Standards are prepared in methanol. These liquid standards are then injected into known volumes of zero air to produce gaseous-phase APH Working and Calibration Standards.

7.1 Reagents

7.1.1 HPLC-grade Water.

7.1.2 High purity purge and trap grade methanol. Store away from other solvents.

7.1.3 Ultra high purity (UHP) helium for the GC/MS system.

7.1.4 Liquid nitrogen for the concentrator system and GC.

7.1.5 Zero air for the concentrator system and standard preparation.

7.2 Stock Standard (Liquid) Solution

7.2.1 Prepare in methanol a stock standard solution of the 30 APH Component Standards at approximately 200 to 500 µg/mL, or purchase certified solutions.

7.2.2 All stock standards must be stored at -20°C in Teflon-lined screw-cap/crimp bottles with minimal headspace.

7.2.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.3 **Primary Dilution (Liquid) Standard**

7.3.1 The stock standard solution is used to prepare a primary dilution standard.

7.3.2 Prior to preparation of the primary dilution standard, rinse a 2 mL volumetric flask with methanol and add approximately 600-800 µL of methanol to the volumetric flask.

7.3.3 Prepare the primary dilution standard at a concentration of approximately 40 µg/mL. Precautions need to be taken to introduce the designated aliquot of stock standard directly into the methanol portion; do not allow the aliquot to run down the sides of the volumetric flask as this may cause some volatility loss of the analytes of interest.

7.3.4 Slowly bring the solvent level to volume by adding methanol to the volumetric flask using a pasteur pipet. Take care not to overshoot the volume mark. Invert the solution three times to thoroughly mix the contents. This is now the completed primary dilution standard solution.

7.3.5 Using a clean pasteur pipet, transfer the primary dilution standard solution to a 2-mL Teflon-lined screw cap amber vial and cap quickly. Label the vial with a relevant number identification and store with minimal headspace in a freezer at -20°C. Reseal the stock solution and return to the freezer.

7.3.6 The primary dilution standard should be replaced at least monthly.

7.4 APH Working (Gaseous) Standards

7.4.1 Prepare gaseous-phase APH Working Standards at a minimum of two concentration levels.

7.4.2 Assemble or purchase appropriate apparatus, valving and systems to allow for the injection of liquid standards and concurrent/subsequent introduction of zero air into evacuated SUMMA® canisters.

7.4.2.1 Verify that an appropriate vacuum exists (-30 inches Hg) in each canister used to prepare working standards.

7.4.2.2 Insert a syringe with a designated aliquot of stock or primary dilution standard into a septum fitted to the inlet of an evacuated canister. Open the canister valve, inject the liquid standard, and then quickly introduce zero air to sweep any remaining vapors in the line into the canister. Within seconds, close the canister valve to seal the canister and then close valving from the zero air source. Repeat this series of steps for any additional liquid standards which may need to be added to the canister.

7.4.2.3 Following the injection of the liquid standards, inject 130 µL of HPLC-grade water into the canister. Open the canister valve, inject the water, and introduce zero air to the canister. Allow the canister to fill with zero air to a final pressure

of 30 psig or 45 psia. This will result in a final humidified gaseous-phase mixture volume of 18 L at standard temperature and pressure (STP).

7.4.2.4 Allow the canister to equilibrate for at least 24 hours.

7.4.3 It is recommended that working standard #1 be prepared by injecting 5 μL of the primary dilution standard (40 μg/mL) into a 6-L canister, which will result in a final gaseous-phase concentration of 11 ng/L at 30 psig (18 L sample volume at STP).

7.4.4 It is recommended that working standard #2 be prepared by injecting 30 μL of the stock standard solution (200 μg/mL) into an 6- L canister, which will result in a final gaseous-phase concentration of 330 ng/L at 30 psig (18 L sample volume at STP).

7.5 APH Calibration (Gaseous) Standards

7.5.1 APH Calibration Standards consist of different volumes of the APH Working Standards that are injected into the concentrator/GC/MS system.

7.5.2 APH Calibration Standards must be injected into the concentrator/GC/MS system at a minimum of 5 different mass levels. One of the mass-injection levels must be at the Reporting Limit. The other mass-injection levels must correspond to the expected range of concentrations found in real world samples or should define the working range of the detector.

7.5.3 The recommended concentrations/mass-injection amounts for the APH Calibration Standards are provided in Table 3

Table 3. APH Calibration Standard Levels

Calibration Level	APH Working Standard (Gaseous) Concentration (μg/mL)	Volume of Injected APH Working Standard (mL)	Resultant Mass of each Component (ng)
1	11	25	0.28
2	11	50	0.55
3	11	100	1.1
4	330	40	13
5	330	100	33
6	330	200	66

7.6 Internal Standards and MS Tuning Standard

The recommended internal standards are Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene d5. The recommended MS tuning standard is 4-bromofluorobenzene (BFB). Prepare or purchase internal standards and the BRB tuning standard as a single gaseous standard at 1.00 ppmV. The internal standards and BFB are loaded onto the sample trap via a 2 mL standard loop on the concentrator system. The corresponding on-column actual ng values of the internal standards and BFB are provided in Table 4 (based upon a 2-mL injection). The amounts of all internal standards have been assigned a nominal value of 10 ng for purposes of quantitation.

Table 4. Amounts of Internal Standards and BFB Tuning Standard

Compound	Concentration (ppmV)	Volume (mL)	On-Column Amount (ng)

Bromochloromethane (Internal Standard#1)	1.00	2.0	11
1,4-Difluorobenzene (Internal Standard #2)	1.00	2.0	9.5
Chlorobenzene-d5 (Internal Standard #3)	1.00	2.0	9.8
BFB (Tuning Standard)	1.00	2.0	15

7.7 **Petroleum Reference Standard**

The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare a gaseous-phase standard by injecting the liquid petroleum reference standard into a pre-cleaned, evacuated 6-liter SUMMA canister, to achieve a total gasoline gaseous concentration of approximately 300 $\mu g/m^3$. Humidify the sample by injecting 130 µL of HPLC water into the canister (at final canister pressure of 30 psig).

8.0 SAMPLE COLLECTION AND HANDLING

8.1 **Canister Cleaning**

All SUMMA® canisters must be certified clean prior to being used for sampling.

8.1.1 Recommended Equipment and Supplies:

8.1.1.1 Flow Manifold – For attaching canisters and conveying flow during evacuation and flushing.

8.1.1.2 Flushing Gas Source – Ultra zero air or Zero Nitrogen (compressed cylinder or on site source) with appropriate cleaning media in line to ensure gas cleanliness.

8.1.1.3 Roughing Pump – For initial evacuation stage.

8.1.1.4 High Vacuum Pump – For final evacuation. Alcatel or equivalent molecular drag recommended. Alternatively, Precision or equivalent oil pump with hydrocarbon traps (i.e., liquid nitrogen) cited by EPA Method TO-14.

8.1.1.5 Controls/Gauges – Control valves or solenoids for enacting cycles. Electronic gauges for measuring rough pressures (in psia or mm Hg) and fine pressure values (millitorrs). Rough vacuum/pressure gauges used for field pressure and vacuum measurements.

8.1.1.6 Humidification Device – Fixture or device to add humidity to canisters and flushing gas during cleaning and batch certification. Water should be Deionized Double Distilled or HPLC grade.

8.1.1.7 Canister Heaters – Heating belts or ovens for heating canisters to 100 degrees C to enhance removal of organic compounds.

8.1.1.8 Laboratory Notebook/Log Book – Used to record dates and canister conditioning actions and certifications.

8.1.2 Recommended Procedures:

8.1.2.1 Empty all canisters to ambient pressure and attach to the manifold. Make sure that there are no leaks.

8.1.2.2 Record canister serial numbers in laboratory notebook.

8.1.2.3 Evacuate with roughing pump to set point (where high vacuum pump can work efficiently) and switch to high vacuum pump. Evacuate canisters to at least 1 torr (1 mm Hg) or below.

8.1.2.4 Flush with humidified clean nitrogen or zero air to 30 psia (1520 mm Hg). Activate heating source and let sit for at least 15 minutes.

8.1.2.5 Turn off heat source and release pressure back to ambient (15 psia).

8.1.2.6 Repeat above steps 2 to 3 times. Note cycle numbers to make sure 3 to 4 cleaning cycles occur. On final cycle, pump down with high vacuum pump to a maximum of 0.05 mm Hg. This pressure would correspond to – 30 inches Hg gauge. Close canister valves prior to turning off high vacuum pump or placing the system in a standby mode.

8.1.2.7 Remove closed canisters from the manifold and check vacuums with a field gauge. They should all read – 30 inches Hg gauge.

8.1.2.8 Remove one canister from the batch exhibiting the highest levels of contamination prior to cleaning (according to the analytical results). Fill this canister to 30 psia with humidified nitrogen or zero air, and analyze it as a Laboratory Method Blank, recording in a laboratory notebook the serial number of this quality control (QC) sample. If any of the Target APH Analytes or hydrocarbon ranges are higher than Reporting Limits, the entire set of canisters must be re-cleaned and recertified. C_{12} hydrocarbons and the naphthalenes may be present at levels up to two times the Reporting Limit.

8.1.2.9 If the Laboratory Method Blank QC canister passes certification, batch canisters should be held for 24 hours prior to issue for field use. Vacuums should be rechecked and canisters with less vacuum than the original reading (after cleaning) should be retained for leak repair.

8.2 Sample Collection and Handling

A recommended Standard Operating Procedure for the collection of air samples is provided in Appendix 4.

8.2.1 All samples must be accompanied by a chain of custody form which documents the canister serial number, date, and time of sample collection.

8.2.2 Samples may be collected as grab samples or as time-integrated samples. Time-integrated samples may be collected for a maximum of 24 hours.

8.2.3 Grab samples are collected by opening the canister valve and allowing the canister to fill to ambient pressure. This process takes approximately one minute.

8.2.4 Time-integrated samples require the use of a properly calibrated flow controller. The flow controller must be calibrated prior to sample collection. Upon receipt at the laboratory, a post sampling calibration check must be performed on the flow controller. The relative percent difference (RPD) between the initial and post sampling calibration readings must be calculated. As long as the RPD is <10%, the calibration is considered to still be valid and thus the sample collection interval is also assumed to be valid. If the RPD is >10%, consideration must be given to whether resampling is necessary to achieve data quality objectives. If the sample is analyzed, a notation must be provided on the data reporting sheet disclosing the RPD value.

8.2.5 Upon receipt at the laboratory, all samples must be assigned unique laboratory identification numbers.

8.2.6 The pressure of all samples upon receipt at the laboratory must be measured and documented. A pressure gauge is attached to the canister inlet, the canister valve is briefly opened and the pressure is recorded. Subambient pressure samples must be pressurized to at least the minimum pressure that will allow the accurate analysis of the sample by the concentration/analytical systems and protocols used by the laboratory. Samples with vacuums less than –10 inches Hg gauge (greater than 10 psia) can be accurately analyzed by some systems, but not on other systems. In all cases, higher pressurization of the samples should be considered for high concentration samples or when replicate analysis is required. Refer to Section 9.5.5 for the calculation of dilution factors due to pressurization of samples.

8.3 Holding Time

The maximum holding time for the analysis of SUMMA® canister samples for APH analyses is **28 days**.

9.0 PROCEDURE

9.1 Sample Preparation and Concentration

9.1.1 Ensure the integrity of the canister sample as described in Section 8.0.

9.1.2 Connect the canister(s) to a Nutech 3600 (or equivalent) autosampler. Place a ¼" stainless steel nut and ferrule on the inlet line facing the canister. Push the inlet line into the orifice of the canister and hold in place while tightening the fitting finger tight. Turn the stainless steel nut ¼ turn more with a wrench. The canister valves should be closed at this point.

9.1.3 Leak check all canister inlet connections. Analysis may not begin until the leak check has passed for each canister being tested.

9.1.4 Open the canister valves.

9.1.5 For the analysis of low concentration samples, set up the system to withdraw approximately 250 mL of air from each canister. If high concentrations are expected, lower volumes may be used.

9.1.6 Recommended concentrator operating parameters are provided in Table 5.

Table 5. Recommended Sample Concentrator Operating Parameters

Inlet purge or sample loop purge time	2.0 minutes
Sample loop equilibrium time	10 seconds
Sample loop load time	Volume dependent
Internal standard loop purge time	1.0 minute
Internal standard equilibrium time	10 seconds
Internal standard load time	1.5 minutes
Cryotrap cool setpoint during sample load	-160°C

Cryotrap desorption setpoint	160 °C
Cryofocus cool setpoint during refocusing	-190°C
Cryofocus desorption setpoint (for injection)	160°C
Sample flow setpoint	30 mL/min
Nafion® dryer temperature during sample loading	0°C
Nafion® dryer temperature during cleanup cycle	125°C
Cryotrap/cryofocus transfer time	2.5 minutes
Cryotrap extended transfer time	5.0 minutes
Nafion® dryer purge flow rate (dehydrates Nafion® membrane)	150 mL/min
Purge gas flow rate (dry purge for low level sample flowpath)	40 mL/min
Autosampler purge flow rate (purges sample flowpaths from	40 mL/min
Loop gas flow rate (transfers sample loop or standard loop contents	20 mL/min
Internal standard flow rate (fills the 2 mL standard loop)	20 mL/min

9.1.6.1 General description of procedure for Nutech 3600 Autosampler: The cryotrap is cooled to the setpoint. The 3600 valve will then rotate to the selected position allowing flow from the canister. The sample purges the inlet and the mass flow controller stabilizes to the sample flow rate. The cryotrap will then be brought in line with the sample path and the sample loading will continue until the target volume is reached. The internal standard will then be introduced to the standard loop, allowed to come to atmospheric pressure, and then transferred to the cryotrap with loop gas. The sample on the cold cryotrap is flushed with helium to purge out residual air and reduce carbon dioxide levels trapped with the sample. The cryofocus is then cooled to the selected setpoint. When the cryofocus reaches its setpoint, the cryotrap is heated and the sample is refocused on the head of the column. When the GC is ready, the sample is injected by ballistic heating of the cryofocuser. The cryotrap stays in line with the GC column for an extended transfer of sample and is then switched out of line for bakeout. The sample dryer cleanup procedure is then used to dehydrate the Nafion® dryer after sample injection.

9.1.7 Modify and implement alternative procedures as necessary when using different autosampler equipment.

9.2 GC/MS Conditions

Gas Chromatograph

9.2.1 Oven program: initial temperature 10°C, hold for 6.0 min. Increase temperature to 135 °C at 3.0°C/min, then increase temperature to 180°C at 10°C/minute. Hold for 6.0 min.

9.2.2 Gas Flows

9.2.2.1 Helium carrier gas flow: 2 mL/min.

9.2.3 Sample Injection

9.2.3.1 Injection mode: splitless.

9.2.3.2 Injection port temperature: 220°C.

9.2.3.3 Inlet pressure: 25.77 psi.

9.2.3.4 Purge flow: 36.3 mL/min at 0 minutes.

9.2.3.5 Gas saver flow: 20 mL/min.

MS Conditions

9.2.4 Temperature of MS/MSD transfer line: 240°C.

9.2.5 Temperature of MS Quad: 150°C.

9.2.6 Temperature of MS Source: 230°C.

9.2.7 Solvent Delay: 4.8 minutes.

9.2.8 Scanning Parameters: 40-250 amu; threshold = 200.

9.3 Retention Time Windows

9.3.1 Before establishing retention time windows, ensure that the GC/MS system is operating within optimum conditions. Analyze an APH Calibration Standard on three separate occasions throughout the course of a 72-hr period. Serial analyses over less than a 72-hr period may result in retention time windows that are too restrictive.

9.3.2 Calculate the standard deviation of the three absolute retention times for each Target APH Analyte, range "marker" compound, internal standard, and MS tuning standard.

9.3.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each analyte of interest. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard approaches zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop an operational retention time window.

9.3.5 The laboratory must calculate retention time windows for each GC column and/or whenever a new GC column is installed. These data must be retained by the laboratory.

9.3.6 The APH retention time (Rt) windows of the aliphatic ranges are defined as beginning 0.1 minutes **before** the Rt of the beginning marker compound and ending 0.1 **after** the Rt of the ending marker compound, except for n-C_9, which is both a beginning and ending marker compound for two different ranges.

The C_5 - C_8 Aliphatic Hydrocarbon range ends immediately (0.01 min) before the elution of the n-C_9 peak. The C_9 - C_{12} Aliphatic Hydrocarbon range begins 0.01 min before the elution of n-C_9, therefore there is no overlap of the two ranges and the n-C_9 peak is only included in the C_9 - C_{12} Aliphatic Hydrocarbon range.

The APH retention time (Rt) window for the C_9 - C_{10} Aromatic Hydrocarbons is defined as beginning 0.1 minutes **after** the Rt of the beginning marker compound and ending 0.1 **after** the Rt of the ending marker compound,

9.3.7 APH marker compounds and windows are summarized in Table 6.

Table 6. APH Range "Marker " Compounds and Range Retention Time Windows

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons	0.1 min. before isopentane	0.01 min. before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons	0.01 min. before n-Nonane	0.1 min. after 1-Methylnaphthalene
C_9-C_{10} Aromatic	0.1 min. after o-xylene	0.1 min. after 1-Methylnaphthalene

9.4 Calibration

9.4.1 The APH Component Standards are used to calibrate the GC/MS system. Two distinct calibration operations are necessary:

9.4.1.1 Target APH Analytes: Relative Response Factors (RRFs) are calculated for the 10 Target APH Analytes and the 3 internal standards, based upon a correlation between the mass of analyte and area counts for the relevant quantitation ions. This allows for the individual identification and quantitation of these specific compounds. IT IS NOT NECESSARY TO DEVELOP RESPONSE FACTORS FOR ANY OTHER INDIVIDUAL APH COMPONENT STANDARD.

9.4.1.2 Collective Aliphatic/Aromatic ranges: Relative Response Factors are calculated for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons based upon a correlation between the TOTAL mass of aliphatic APH Component Standards eluting within the range of interest and the total ion area count. A Relative Response Factor is calculated for C_9-C_{10} Aromatic Hydrocarbons based upon a correlation between the TOTAL mass of aromatic APH Component Standards eluting within this range and the total area count of extracted ions 120 and 134. Specified APH Component Standards are designated "marker" compounds to define the beginning and end of the hydrocarbon ranges.

9.4.2 Primary and secondary extracted ions for all APH Component Standards and recommended internal standards are provided in Table 7. The recommended internal standards and associated Target APH Analyte and Hydrocarbon Ranges are provided in Table 8. A listing of analytes used to establish response factors for each hydrocarbon range of interest, and the mass-injection amounts of the APH Component Standards eluting in these ranges are provided in Table 9.

Table 7. Primary (Quantitation) & Secondary Ions for APH Component/Internal Standards

APH Component Standard	CAS Number	Target APH Analyte	Quantitation Ion	Secondary Ion(s)
Bromochloromethane (IS1)	74975		128	49, 130
1,3-Butadiene	106990	✓	54	53, 50
Isopentane	78784		43	42, 41, 57
Methyl-tert-butylether	1634044	✓	73	45
n-Hexane	110543		57	41, 43, 56
Cyclohexane	110827		56	84, 41
1,4-Difluorobenzene (IS2)	540363		114	63
2,3-Dimethylpentane	565593		56	43, 57, 41
Benzene	71432	✓	78	52, 51
n-Heptane	142825		43	71, 57, 100
Toluene	108883	✓	91	92
Chlorobenzene-d5 (IS3)	3114554		117	119, 82
n-Octane	111659		43	85, 57, 71
2,3-Dimethylheptane	3074713		43	84, 85
Ethylbenzene	100414	✓	91	106
m-Xylenes	108383	✓	91	106, 105
p-Xylenes	106423	✓	91	106, 105
n-Nonane	111842		43	57, 85
o-Xylene	95476	✓	91	106, 105
Isopropylbenzene	98828		105	120
1-Methyl-3-ethylbenzene	620144		105	120
1,3,5-Trimethylbenzene	526738		105	120
n-Decane	124185		57	43, 71, 85
Butylcyclohexane	1678939		83	55, 82
p-Isopropyltoluene	99876		119	105, 134
1,2,3-Trimethylbenzene	526738		105	120
Indene	95136		115	116
n-Undecane	1120214		57	43, 71, 85
n-Dodecane	112403		57	43, 71, 85
Hexylcyclohexane	4292755		83	82, 55
Naphthalene	91203	✓	128	
2-Methylnaphthalene	91576	✓	142	141, 115
1-Methylnaphthalene	90120		142	141, 115

NOTE: All APH Component Standards are listed in Table 7 for reference purposes. Only the RRFs for Target APH Analytes and Internal Standards need to be determined on a compound-specific basis

Table 8. Internal Standards and Associated Target APH Analytes and Hydrocarbon Ranges

Bromochloromethane (IS #1)	1,4-Difluorobenzene (IS #2)	Chlorobenzene-d5 (IS #3)
1,3-Butadiene Methyl-tertbutylether	Benzene Toluene C_5-C_8 Aliphatics	Ethylbenzene m&p-Xylenes o-Xylene Naphthalene 2-Methylnaphthalene C_9-C_{12} Aliphatics C_9-C_{10} Aromatics

Table 9. Mass Injections of APH Component Standards for the Hydrocarbon Ranges for Initial Calibration.

Range	APH Component Standards used to Establish Range Response Factor	Calib Level	Working Std conc (µg/mL)	Volume Working Std (mL)	Mass of each Component Standard (ng)	Mass of all Component Standards (ng)
C_5-C_8 Aliphatic Hydrocarbons	Isopentane n-Hexane Cyclohexane 2,3-Dimethylpentane n-Heptane n-Octane	1	11.1	25	0.28	1.68
		2	11.1	50	0.56	3.36
		3	11.1	100	1.11	6.66
		4	333.3	40	13.3	79.8
		5	333.3	100	33.3	199.8
		6	333.3	200	66.7	400.2
C_9-C_{12} Aliphatic Hydrocarbons	2,3-Dimethylheptane[a] n-Nonane n-Undecane n-Dodecane Butylcyclohexane[b] Hexylcyclohexane	1	11.1	25	0.28	2.52[a,b]
		2	11.1	50	0.56	5.04[a,b]
		3	11.1	100	1.11	9.99[a,b]
		4	333.3	40	13.3	119.7[a,b]
		5	333.3	100	33.3	299.7[a,b]
		6	333.3	200	66.7	600.3[a,b]
C_9-C_{10} Aromatic Hydrocarbons	Isopropylbenzene 1-Methyl-3-ethylbenzene 1,3,5-Trimethylbenzene 1,2,3-Trimethylbenzene p-Isopropyltoluene Indene	1	11.1	25	0.28	1.68
		2	11.1	50	0.56	3.36
		3	11.1	100	1.11	6.66
		4	333.3	40	13.3	79.8
		5	333.3	100	33.3	199.8
		6	333.3	200	66.7	400.2

[a] 2,3-dimethylheptane co-elutes with m&p-xylenes; total amount C_9-C_{12} aliphatics also includes m&p-xylenes.
[b] butylcyclohexane co-elutes with indene; total amount C_9-C_{12} aliphatics also includes indene.

Initial Calibration

9.4.3 Perform initial calibration at a minimum of five different mass-injection levels by analyzing various volumes of the APH Working Standards. Recommended concentrations of calibration standards are provided in Table 3**. The lowest calibration standard must be at or below the Reporting Limit**. If the response for the Target APH Analytes is not linear at the lowest level for the higher molecular weight compounds, this point should not be included in the calibration curve for these compounds. As a result, the analysis of more than five levels may be required in order to ensure a minimum of five calibration points for each analyte.

9.4.4 Analyze each calibration standard according to the procedures specified in Sections 9.1 and 9.2.

9.4.5 Target APH Analytes - Tabulate the area response of the characteristic ions against the mass of each Target APH Analyte and internal standard and calculate relative response factors (RRFs) for each compound using equation 1. Perform this calculation for each Target APH Analyte.

Equation 1: Relative Response Factor for Target APH Analytes

$$RRF = [(A_{EC})*(C_I)] / [(A_{EI})*(C_c)]$$

where:

RRF = relative response factor
A_{EC} = area count of the extracted ion for the analyte of interest
C_I = mass of internal standard (ng)
A_{EI} = area count of the extracted ion for the associated internal standard
C_C = mass of analyte of interest (ng)

9.4.6 Hydrocarbon Ranges - Establish retention time windows for the hydrocarbon ranges using the APH Component "marker compounds" shown in Table 6.

9.4.7 Calculate a response factor for the C_5-C_8 Aliphatic Hydrocarbon range using the following steps.

9.4.7.1 Using total ion integration, sum the individual peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_5-C_8 Aliphatic Hydrocarbons, as designated in Table 9. Do not include the peak areas of internal/tuning standards.

9.4.7.2 Using the total area generated in Section 9.4.7.1, calculate the Range RRF using Equation 2.

Equation 2: Relative Response Factor for C_5-C_8 Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI2})*(C_T)]$$

where:

Range RRF = relative response factor for the hydrocarbon range
A_T = total ion area count of the six aliphatic APH Component Standards which elute within this range (see Table 9)

C_I = mass of internal standard #2, ng (1,4-Difluorobenzene)
A_{EI2} = area count of the extracted ion for internal standard #2
C_T = summation of the masses of the six aliphatic APH Component Standards (ng) which elute within this range (see Table 9)

9.4.8 Calculate a response factor for the C_9-C_{12} Aliphatic Hydrocarbon range using the following steps.

9.4.8.1 Using total ion integration, sum the individual peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_9-C_{12} Aliphatic Hydrocarbons, as designated in Table 9. Do not include the peak areas of internal/tuning standards.

9.4.8.2 Using the total area generated in Section 9.4.8.1, calculate the Range RRF using Equation 3.

Equation 3: Relative Response Factor for C_9-C_{12} Aliphatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI3})*(C_T)]$$

where:

Range RRF = relative response factor for the hydrocarbon range
A_T = total ion area count of the six aliphatic APH Component Standards which elute within this range (see Table 9)
C_I = mass of internal standard #3, ng (Chlorobenzene d5)
A_{EI3} = area count of the extracted ion for internal standard #3
C_T = summation of the masses of the six aliphatic APH Component Standards (ng) which elute within this range, **plus the summation of the 3 aromatic APH Component Standards (ng) which co-elute with the aliphatic standards** (see Table 9)

9.4.9 Calculate a response factor for the C_9-C_{10} Aromatic Hydrocarbon range using the following steps.

9.4.9.1 Using extracted ion 120, sum the individual peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_9-C_{10} Aromatic Hydrocarbons, as designated in Table 9. Do not include the peak areas of internal/tuning standards.

9.4.9.2 Using extracted ion 134, sum the peak areas of the six (6) APH Component Standards that are used to establish an average range response factor for C_9-C_{10} Aromatic Hydrocarbons, as designated in Table 9. Do not include the peak areas of internal/tuning standards.

9.4.9.3 Sum the area counts from Sections 9.4.9.1 and 9.4.9.2.

9.4.9.4 Using the area count generated in 9.4.9.3, calculate the RRF using Equation 4.

Equation 4: Relative Response Factor for C_9-C_{10} Aromatic Hydrocarbons

$$\text{Range } RRF = [(A_T)*(C_I)] / [(A_{EI3})*(C_T)]$$

where:

Range RRF = relative response factor for the hydrocarbon range
A_T = summation of area counts using extracted ions 120 and 134
C_I = mass of internal standard #3, ng (Chlorobenzene d5)
A_{EI3} = area count of the extracted ion for internal standard #3
C_T = summation of the masses of the six aromatic APH Component Standards (ng) which elute within this range (see Table 9)

9.4.10 Calculate the average response factor for each of the Target APH Analytes and each hydrocarbon range.

9.4.11 Calculate the percent relative standard deviation (%RSD) of the response factors over the working range of the curve for each of the Target APH Analytes and each hydrocarbon range using Equation 5.

Equation 5: Percent Relative Standard Deviation

$$\%RSD = [(SD_{n-1}) / (AVG_X)]*100]$$

where:

%RSD = percent relative standard deviation
SD_{n-1} = standard deviation (n-1 degrees of freedom)
AVG_x = average response factor from the initial calibration curve

9.4.11.1 If the %RSD is ≤30, linearity can be assumed for the associated Target APH Analyte or hydrocarbon range.

9.4.11.2 If the %RSD >30, a calibration curve (linear regression or quadratic) should be generated. The correlation coefficient for the calibration curve should be greater than 0.99.

9.4.12 The initial calibration must be verified through the analysis of a Laboratory Control Spike. This analysis must be performed every time an initial calibration is performed.

9.4.12.1 The Laboratory Control Spike must be prepared by spiking an evacuated SUMMA® canister with a different stock standard solution than that used for calibration. The standard should be prepared near the midpoint of the calibration curve.

9.4.12.2 The spike recovery must be between 70% and 130%.

9.4.12.3 At a minimum, the Laboratory Control Spike must contain 1,3-butadiene, benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, and at least one compound from each individual stock standard purchased from a vendor (as applicable).

Continuing Calibration

9.4.13 A continuing calibration check must be performed daily prior to sample analysis.

9.4.14 Analyze an APH Calibration Standard which is near the midpoint of the calibration curve.

9.4.15 If the %RSD for a Target APH Analyte or hydrocarbon range was ≤30 in the initial calibration, calculate the response factor for this analyte or hydrocarbon range from the continuing calibration standard.

9.4.15.1 Calculate the percent difference (%D) of the continuing calibration response factor from the initial calibration average response factor using Equation 6.

Equation 6: Percent Difference

$$\%D = [(RF_C) - (RF_I)] / [(RF_I)] * 100$$

where:

%D = percent difference
RF_C = response factor from the continuing calibration standard
RF_I = average response factor from the initial calibration curve

9.4.16 If the %RSD for a Target APH Analyte or hydrocarbon range was >30 in the initial calibration and a calibration curve (linear regression or quadratic) was used, calculate the actual mass (ng) of this analyte or hydrocarbon range using the calibration curve.

9.4.16.1 Calculate the percent recovery (%R) of the Target APH Analyte or hydrocarbon range using Equation 7.

Equation 7: Percent Recovery

$$\%R = [(C_{found}) / (C_{true})] * 100$$

where:

%R = percent recovery
C_{found} = mass of the analyte or hydrocarbon range detected in the standard (ng)
C_{true} = true mass of the analyte or hydrocarbon range in the standard (ng)

9.4.17 The %Ds must be <30 and/or the %Rs must fall between 70 and 130. If more than four compounds fail to meet these criteria, or if the %D for any one compound is greater than 50, or if the %R for any one compound is <50 or >150, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

Retention Time Windows

9.4.18 The relative retention time (RRT) and RRT window for each Target APH Analyte, internal standard, and hydrocarbon range "marker" compound must be established on a daily basis. The RRT for each analyte of interest shall be established as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3

Daily GC/MS Performance Check

9.4.19 A check of the GC/MS tuning must be performed daily prior to sample analysis. The GC/MS system is checked to confirm that acceptable performance criteria for mass

spectral abundance ratios are met for 4-bromofluorobenzene (BFB) These criteria must be met prior to analyzing further standards, blanks and samples.

9.4.20 The BFB spectrum must meet the criteria in Table 2. If the BFB spectrum does not meet these criteria, the analysis must be repeated. If the BFB spectrum still does not meet these criteria, the GC/MS instrument must be retuned.

9.5 GC/MS Analysis

9.5.1 Program the Nutech 3550A concentrator (or equivalent) to the specific analytical conditions listed in Table 5 and the GC/MS parameters listed in Section 9.2.

9.5.2 Perform an initial calibration or continuing calibration check. Evaluate the BFB spectrum of the first standard that is analyzed.

9.5.3 Analyze 250 mL of a Laboratory Method Blank. The method blank must be free of Target APH Analyte contamination at or above the Reporting Limit, except that C_{12} hydrocarbons and naphthalenes may be present at levels up to two times the Reporting Limit.

9.5.4 Preconcentrate a 250-mL aliquot of sample on the concentrator and inject it onto the GC column.

9.5.5 Dilutions and Sub-Atmospheric Samples

9.5.5.1 For dilutions, smaller sample volumes (<250 mL) are analyzed. The smallest volume which can be analyzed with accuracy is 20 mL. For more concentrated samples, use a 5 mL sample injection and bypass the Nafion® dryer. The dilution factor is accounted for by entering the volume analyzed in the sample calculation discussed in Section 9.6.

9.5.5.2 Samples which arrive at the laboratory with high vacuum levels must be pressurized with zero air, as discussed in Section 8.2.6. This pressurization results in a dilution factor. The dilution factor is calculated using Equation 8.

Equation 8: Dilution Factor for Pressurization of Subatmospheric Samples: Three Steps

Step 1: Calculate the volume in the (6-liter) canister prior to pressurization.

$$V_{ci} = 6 * [(30 - |P_I|) / 30]$$

Step 2a: Calculate the volume in the canister after pressurization.

If final pressure is <0 psig:

$$V_{cf} = 6 * [(30 - |P_F|) / 30]$$

Step 2b: Calculate the volume in the canister after pressurization.

If final pressure is >0 psig:

$$V_{cf} = 6 + (P_F / 15 * 6)$$

Step 3: Calculate the dilution factor.

$$DF = V_{cf} / V_{ci}$$

where:

V_{ci} = volume of air in canister prior to pressurization
P_I = pressure reading of canister prior to pressurization (absolute value)
V_{cf} = volume of air in canister after pressurization
P_F = pressure reading of canister after pressurization (absolute value)
DF = dilution factor

Qualitative Identifications

9.5.6 The Target APH Analytes must be identified by an analyst competent in the interpretation of chromatograms and mass spectra. Two criteria must be satisfied to verify the identification: (1) elution of the component in the sample at the same GC relative retention time (RRT) as the component in the standard, and (2) agreement of the sample component and standard component mass spectra.

9.5.7 If co-elution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned using extracted ion current profiles for the ion unique to the component of interest.

9.5.8 For comparison of the standard and sample component mass spectra, mass spectra of standards obtained on the GC/MS under the same instrument conditions are required. Once obtained, these standard spectra may be used for identification and reference purposes. The requirements for qualitative verification by comparison of mass spectra are as follows:

9.5.8.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

9.5.8.2 The relative intensities of ions specified must agree within ±20% between the standard and sample spectra.

9.5.8.3 Ions greater than 10% in the sample spectrum must be considered and accounted for by the analyst making the comparison.

9.5.9 The primary and secondary ions for all APH Component Standards are provided in Table 7.

9.6 Calculations

9.6.1 Individual Target APH Analytes: The average response factor from the initial calibration is used to calculate the amount of analyte detected in the sample. Equation 9 is used to

calculate the mass of sample analyte in ng. Equation 10 is used to convert ng to μg/m^3. Equation 11 is used to convert of μg/m^3 to ppbV.

Equation 9: Calculation of Analysis Results in ng

$$ng = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})]$$

where:

A_x = area of quantitation ion for the Target APH Analyte (see Table 7)
C_{IS} = mass of the internal standard
A_{IS} = area of quantitation ion for the associated internal std (see Table 7)
RRF_{avg} = average response factor for the specific compound to be measured**

**NOTE: The amounts (ng) of Target APH Analytes must be calculated from the calibration curve (linear regression or quadratic), if utilized in the initial calibration.

Equation 10: Conversion of ng to μg/m^3

$$\mu g / m3 = (ng / VA) * DF$$

where:

V_A = volume of sample analyzed (liters)
DF = dilution factor; if no dilution was made, the dilution factor =1

Equation 11: Conversion of μg/m^3 to ppbV

$$ppbV = (\mu g / m3) * 24.47 / MW$$

where:

MW = molecular weight of the compound of interest, g/mol (see Table 1 for a list of the molecular weights of the Target APH Analytes)

9.6.2 The integration of Target APH Analytes and internal standards should be performed from valley to valley.

9.6.3 Hydrocarbon Ranges: The average range response factor from the initial calibration is used to calculate the mass (ng) of range hydrocarbons in samples**. Collective peak area integration for the hydrocarbon ranges must be from baseline (i.e., must include the unresolved complex mixture).**

C_5-C_8 Aliphatic Hydrocarbons

9.6.3.1 Using total ion integration, sum all peaks in the appropriate retention time window as specified in Sections 9.3 and Table 6.

9.6.3.2 From this sum, subtract the total ion area counts of all internal standards which elute in this range (all of the recommended internal standards elute in this range).

9.6.3.3 Calculate a preliminary mass amount in ng using Equation 12.

Equation 12: Calculation of Preliminary Sample Analysis Results (ng)

$$ng = [(A_x) * (C_{IS})] / [(A_{IS}) * (RRF_{avg})]$$

where:

A_x = total ion area count of all peaks eluting within C5-C8 Aliphatic Hydrocarbon range window
C_{IS} = mass of the internal standard, ng
A_{IS} = area of quantitation ion for internal standard #2 (1,4-Difluorobenzene)
RRF_{avg} = average range response factor for the C5-C8 Aliphatic Hydrocarbon range

9.6.3.4 From the preliminary amount (ng), calculate an adjusted mass amount of range hydrocarbons by subtracting the masses of Target APH Analytes which elute in this range (typically MtBE, benzene, toluene, and ethylbenzene).

9.6.3.5 Convert the adjusted ng value to μg/m^3 using Equation 13.

Equation 13: Conversion of ng to μg/m^3

$$\mu g / m^3 = (C_{ng} / V_A) * DF$$

where:

C_{ng} = adjusted total mass of range hydrocarbons in ng
V_A = volume of sample analyzed (liters)
DF = dilution factor; if no dilution was made, the dilution factor = 1.

C_9-C_{10} Aromatic Hydrocarbons

9.6.3.6 Using extracted ion 120, sum all peaks in the appropriate retention time window as specified in Section 9.3 and Table 6.

9.6.3.7 Using extracted ion 134, sum all peaks in the appropriate retention time window as determined in Section 9.3 and Table 6.

9.6.3.8 Sum the areas of ions 120 and 134.

9.6.3.9 Calculate an amount in ng using Equation 12, using the summed areas of ions 120 and 134

9.6.3.10 Convert the ng value to μg/m^3 using Equation 13.

C_9-C_{12} Aliphatic Hydrocarbons

9.6.3.11 Using total ion integration, sum all peaks in the appropriate retention time window as specified in Section 9.3 and Table 6.

9.6.3.12 From this sum, subtract the total ion area counts of the 4-bromofluorobenzene peak (and any internal standards which elute in this range).

9.6.3.13 Calculate a preliminary mass amount in ng using Equation 12.

9.6.3.14 From the preliminary amount (ng), calculate an adjusted mass amount of range hydrocarbons by subtracting the masses of Target APH Analytes which elute in this range (typically m-xylene, p-xylene, o-xylene, naphthalene, 2-methylnaphthalene), **and by subtracting out the mass amount of C_9-C_{10} Aromatic Hydrocarbon**s.

9.6.3.15 Convert the ng value to $\mu g/m^3$ using Equation 13.

10.0 QUALITY CONTROL

10.1 **General Requirements and Recommendations**

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of prepared QC samples to evaluate and document the quality of data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method.

10.1.2 The internal standard area counts of each sample, blank, and Laboratory Control Spike must be evaluated against the corresponding continuing calibration standard. The internal standard area counts must be within 50-200% of the continuing calibration standard area counts. If the internal standards fall outside this range, the sample, blank, or Laboratory Control Spike must be reanalyzed.

10.1.3 Tuning checks of the MS must occur each day that analyses are conducted. An acceptable spectrum for the recommended tuning standard BFB is provided in Table 1.

10.1.4 A Laboratory Method Blank must be run after samples suspected of being highly contaminated to determine if sample carryover has occurred. If samples have been analyzed using an autosampler, data should be evaluated for potential carryover and reanalysis conducted, as appropriate.

10.1.5 At a minimum, for each day of analysis, a Calibration Check Standard, Laboratory Method Blank, and duplicate sample must be run. For analytical batches with more than 10 samples, the analysis of an additional mid-range Calibration Check Standard should also be considered.

10.1.6 The recommended sequence of analysis is as follows:

10.1.6.1 Calibration Standards (initial) or mid-range Calibration Check Standard (daily check of initial calibration), either of which are used to evaluated GC/MS tuning [REQUIRED]

10.1.6.2 Laboratory Control Spike [REQUIRED after initial calibration/recalibration]

10.1.6.3 Laboratory Method Blank [REQUIRED]

10.1.6.4 Samples

10.1.6.5 Duplicate sample [REQUIRED]

10.1.6.6 Mid-range Calibration Check Standard [consider after 10 samples, as appropriate]

10.1.7 All analytical sequences and data must be recorded in a daily run log.

10.2 **Minimum Instrument QC**

10.2.1 Internal standards used must be adequately resolved from individual compounds in the APH Component Standard.

10.2.2 Retention time windows and Relative Retention Times (RRTs) must be established for each analyte and hydrocarbon range of interest each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Section 9.3)

10.2.3 Calibration curves must be developed based upon the analysis of calibration standards prepared at a minimum of 5 mass-injection levels. The linearity of calibration or response factors may be assumed if the percent relative standard deviation (%RSD) over the working range of the curve is less than or equal to 25%. Alternatively, if linear regression analysis is used for quantitation, the correlation coefficient (r) must be at least 0.99. (See Section 9.4)

10.3 **Initial and Periodic Method QC Demonstrations**

The procedures specified in Section 10.3.1 through 10.3.3 must be conducted as an initial demonstration of laboratory capability, prior to the analysis of any samples. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, and/or in response to confirmed or suspected systems, method, or operational problems.

10.3.1 Accuracy and Precision

10.3.1.1 To demonstrate initial laboratory capability, analyze a minimum of four replicate samples obtained from a humidified canister fortified with each Target APH Analyte at approximately 20 – 30 $\mu g/m^3$ (3 – 10 ng of on-column mass injection).

10.3.1.2 Calculate the measured concentrations of each analyte in all replicates, the mean accuracy (as a percentage of true value) for each analyte, and the precision (as %RSD) of the measurements for each analyte.

10.3.1.3 For each analyte, the mean accuracy, expressed as a percentage of the true value, must be between 70% and 130%, and the %RSD must be less than or equal to 25. Lower recoveries are permissible for MtBE, naphthalene and 2-methylnaphthalene.

10.3.1.4 If desired, the Accuracy and Precision evaluation may be combined with the MDL evaluation specified in Paragraph 10.3.2.

10.3.2 Method Detection Limits for Target APH Analytes

Analyze a minimum of seven replicate samples obtained from a canister fortified with all Target APH Analytes of interest at 3 to 5 times the calculated or estimated Instrument Detection Limits (IDLs). Typical spiking concentrations for analytes of interest are between 10 and 15 $\mu g/m^3$ (1.5 – 5 ng on-column mass injection). Analyze each replicate

according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL), Minimum Level (ML) and Reporting Limit (RL) of each analyte using the procedures described in Section 12.0.

10.3.2.1 For each analyte, excluding MtBE, naphthalene, and 2-methylnaphthalene, the mean accuracy, expressed as a percentage of the true value, must be between 70% and 130%. For each analyte, the %RSD of replicate samples must be less than or equal to 25.

10.3.2.2 For naphthalene and 2-methylnaphthalene, the mean accuracy, expressed as a percentage of the true value, must be between 50% and 150%. For MtBE, the mean accuracy, expressed as a percentage of the true value, must be between 25% and 150%.

10.3.3 Method Detection Limits for Hydrocarbon Ranges

Analyze a minimum of seven replicate samples obtained from a humidified canister fortified with a petroleum reference standard (gasoline) at 3 to 5 times the calculated or estimated Instrument Detection Limit (IDL). Typical gasoline spiking concentrations are 300 – 400 $\mu g/m^3$. Analyze each replicate according to the procedures described in Section 9.0. Calculate the Method Detection Limit (MDL), Minimum Level (ML) and Reporting Limit (RL) of each hydrocarbon range using the procedures described in Section 12.0.

10.3.3.1 The mean recovery of the summation of all Target APH Analytes and all three hydrocarbon ranges, expressed as a percentage of the true value of the petroleum reference standard, must be between 70% and 130%. For each hydrocarbon range, the %RSD must be less than or equal to 25.

10.3.4 Ongoing Method QC Demonstrations

At a minimum, for each day of analyses, the laboratory must analyze the following:

10.3.4.1 **Calibration Check Standard** - A mid-range calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range calibration check standard is recommended after the analysis of the tenth sample. For analytes of interest, the percent difference (%D) must be <30 and/or the percent Recovery (%R) must fall between 70 and 130. If more than four compounds fail to meet this criteria, or if the %D for any one compound is greater than 50, or if the %R is <50 or >150 for any one compound, the instrument must be recalibrated. Otherwise, sample analysis may proceed.

10.3.4.2 **Laboratory Method Blank** – A humidified canister pressurized with zero air is utilized as a Laboratory Method Blank. The Laboratory Method Blank must be free of Target APH Analyte contamination at or above the Reporting Limit. C_{12} hydrocarbons and the naphthalenes may be present at up to two times the Reporting Limit.

10.3.4.3 **Sample Duplicate** – The relative percent difference (RPD) of duplicate sample analyses must not exceed 30. If the RPD exceeds 30, the sample analysis must be repeated. If an analyte is detected in one analysis at >5 times the Reporting Limit and not detected in the duplicate analysis, the analysis must be repeated. If an analyte is detected in one analysis at <5 times the Reporting Limit and not detected in the duplicate analysis, the RPD is not calculable and the analysis

does not have to be repeated. If an analyte is not detected in both the original and duplicate analyses, the RPD is not calculable. Equation 14 is used to calculate the RPD.

Equation 14: RPD Calculation

$$RPD = (C_s - C_d) / [(C_s + C_d) / 2] * 100$$

where:

RPD = relative percent difference
C_s = concentration in original sample analysis
C_d = concentration in duplicate sample analysis

10.3.5 If any of the performance standards specified in Section 10.3.4 are not met, the problem must be corrected before further samples are analyzed. Any samples run between the last QC samples that meet the criteria and those that are fallen out must be rerun. If this is not possible, that data must be reported as suspect.

10.3.6 The analyte and hydrocarbon range Reporting Limits should be verified/re-established at least once per year, or upon a major change in system equipment or operations.

11.0 DATA PRODUCTION AND REPORTING

11.1 The required data reporting format is presented in Appendix 3. The purpose of this format is to provide data users with a succinct and complete summary of pertinent information and data, a clear indication of whether significant modifications were made to the APH Method, and a clear affirmation on whether the QA/QC procedures and standards specified in this method were followed and achieved. While it is permissible to alter the form and presentation of the data, all of the information must be provided in a clear, concise, and succinct manner.

11.2 "Significant Modifications" to this method shall include, without limitation, all of the following:

11.2.1 The use of sample collection devices other than evacuated SUMMA® canisters;

11.2.2 The use of alternative detectors to quantitate Target APH Analytes and/or hydrocarbon range concentrations;

11.2.3 The use of extracted ions other than 120 and 134 to quantitate C_9-C_{10} Aromatic Hydrocarbons; or

11.2.4 The failure to provide all of the data and information required in the reporting format presented in Appendix 3.

11.3 Positive affirmation that all required QA/QC procedures and performance standards were followed and achieved means that all of the required steps and procedures detailed in Section 10.0 have been followed, and that all data obtained from these steps and procedures were within the acceptance limits specified for these steps and procedures.

12.0 REPORTING LIMITS

12.1 Each laboratory using this method shall experimentally determine the Reporting Limits (RLs) for each Target APH Analyte and hydrocarbon range. Although laboratories have flexibility in

performing this task, in order to ensure the validity and meaningfulness of these concentration values, the following performance standards must always be achieved:

12.1.1 The RLs for individual analytes must be established by the analyses of at least 7 replicate samples from a canister fortified with the analytes of interest;

12.1.2 The RLs for the hydrocarbon ranges must be established by the analyses of at least 7 replicate samples from a canister fortified with a petroleum reference standard;

12.1.3 The RL for individual analytes may be set no lower than the lowest calibration standard which is still within the linear range of the calibration curve (i.e., less than 25% RSD); and

12.1.4 The RL for individual analytes must be verified by the analyses of at least 4 replicate samples from a canister fortified at the Reporting Limit, where the precision of replicate analyses is demonstrated to be equal to or less than 25% RSD, and the mean accuracy is demonstrated to be between 70-130% of the spiked value.

12.2 **Target APH Analytes**

12.2.1 The Reporting Limits (RLs) for the Target APH Analytes should be calculated by first determining a Method Detection Limit (MDL) for each analyte, and then applying an adjustment factor to the MDL to calculate the Minimum Level (ML).

12.2.2 The MDL is determined by the analysis of 7-10 replicate samples, as detailed in Section 10.3.2. The data obtained from these analyses are then use to calculate the MDL using Equation 15.

Equation 15

$$MDL = (t) \times (SD)$$

where:

t = student t value at the 99% confidence level.
SD = standard deviation of the replicate analysis.

Student t values are as follows:

Number of replicates	t value
7	3.14
8	3.00
9	2.90
10	2.82

12.2.3 The Minimum Level (ML) is then calculated from the MDL according to equation 16:

Equation 16

$$ML = (MDL) \times (3.18)$$

12.2.4 If the ML is greater than the concentration of analyte used in the MDL study, the Reporting Limit is this value. If the ML is less than the concentration of analyte used in the MDL study, the laboratory may either (a) establish the RL at the concentration of the analyte used in the MDL study, or (b) undertake additional analyses to demonstrate method performance at the ML.

12.2.4.1 To demonstrate adequate method performance at the calculated ML and proposed RL, analyze at least 4 replicate samples from a canister fortified with the analytes of interest at the ML.

12.2.4.2 The mean recovery of each analyte, expressed as a percentage of the true value, must be between 70-130%. For each analyte, the %RSD of replicate analyses must be less than or equal to 25%.

12.2.5 If necessary, a low-level calibration standard must be prepared at the concentration of the proposed RL. This standard must be analyzed and shown to be within the linear range of the calibration curve (i.e., %RSD equal to or less than 25

12.3 Collective Hydrocarbon Ranges

12.3.1 The Reporting Limit (RL) for each hydrocarbon range should be calculated by first determining a Method Detection Limit (MDL) for each range, and then applying an adjustment factor to the MDL to calculate the Minimum Level (ML).

12.3.2 The MDL is determined by the analysis of 7-10 replicate samples, as detailed in Section 10.3.3. The data obtained from these analyses are then use to calculate the MDL using Equation 14.

12.3.3 The Minimum Level (ML) is then calculated from the experimentally determined MDL according to equation 16.

12.3.4 If the ML is greater than the mean concentration of the hydrocarbon range determined in the MDL study, the Reporting Limit is this value. If the ML is less than the mean concentration of the hydrocarbon range determined in the MDL study, the laboratory may either (a) establish the RL at the mean concentration of the hydrocarbon range determined in the MDL study, or (b) undertake additional analyses to demonstrate method performance at the ML.

12.3.4.1 To demonstrate adequate method performance at the calculated ML and proposed RL, analyze at least 4 replicate samples from a canister fortified with the

petroleum reference standard at or near the ML. For range MLs, this will involve assumptions on the chemistry of the petroleum reference standard, based upon data obtained during the MDL studies.

12.3.4.2 The mean recovery of the summation of all Target APH Analytes and all three hydrocarbon ranges, expressed as a percentage of the true value of the petroleum reference standard, must be between 70% and 130%. For each hydrocarbon range, the %RSD must be less than or equal to 25%.

13.0 METHOD PERFORMANCE

Single laboratory accuracy, precision and MDL data for method analytes are provided in Appendix 1. Chromatograms are provided in Appendix 2.

14.0 REFERENCES

1. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, US EPA, EPA-600/4-84-041, 1987. Research Triangle Park, NC.

2. *Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air*, ENSR Corporation, June 1999.*

3. *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH),* Massachusetts Department of Environmental Protection, January 1998.*

4. *Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*, Massachusetts Department of Environmental Protection, August, 1994.*

5. *Report on Results of the Fall 1997 VPH/EPH Round Robin Testing Program*, Massachusetts Department of Environmental Protection, January 12, 1998.*

* available at http://www.magnet.state.ma.us/dep/bwsc/vph_eph.htm

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION AND METHOD DETECTION LIMITS (MDL) DATA

(To be included in Final Method)

See *Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air*(199), available at http://www.magnet.state.ma.us/dep/bwsc/vph_eph.htm

APPENDIX 2

CHROMATOGRAMS

(To be included in Final Method)

See *Laboratory Method Validation Study for the Determination of Volatile Petroleum Hydrocarbons in Indoor Air*(199), available at http://www.magnet.state.ma.us/dep/bwsc/vph_eph.htm

Appendix 3: REQUIRED APH DATA REPORTING FORMAT/INFORMATION

SAMPLE INFORMATION (check all that apply)

Sample Type(s)	► Grab ► Time-integrated: ► 2 hour ► 4 hour ► 8 hour ► 24 hour ► Other:
Sample Container(s)	► SUMMA® canister(s): ► 6-L ► 15-L ► Other:
Sampling Flow Controller(s)	► Mechanical ► Fixed-Orifice ► Electronic ► Other:
Sampling Flow Meter(s)	Relative Percent Difference of pre & post-sampling calibration check(s): ► ≤ 10% ► > 10%
Sample Zone(s) [Appendix 4]	► Zone A ► Zone A-1 ► Zone B ► Zone C ► Zone D ► Zone E ► Outside ►

APH ANALYTICAL RESULTS

Method: Public Comment Draft 1.0		**Client ID**					
Internal Standards:		**Lab ID**					
		Date Collected					
		Date Received					
		Date Analyzed					
		Pre-sample press			**psig**		**psig**
MS Tuning Standard:		**Post-sample press**			**psig**		**psig**
		Pre-analysis press			**psig**		**psig**
		Dilution Factor					
Target APH Analytes & Hydrocarbon Ranges	**Range in which Analyte elutes**	**Reporting Limit**		**Sample Results**		**Sample Results**	
		µg/m³	**ppb v/v**	**µg/m³**	**ppb v/v**	**µg/m³**	**ppb v/v**
Unadjusted C5-C8 Aliphatics[1]	**N/A**						
Unadjusted C9-C12 Aliphatics[1]	**N/A**						
1,3-Butadiene							
Methyl-tert-butylether							
Benzene							
Toluene							
Ethylbenzene							
m- & p- Xylenes							
o-Xylene							
Naphthalene							
2-Methylnaphthalene							
C5-C8 Aliphatic Hydrocarbons[1,2]	**N/A**						
C9-C12 Aliphatic Hydrocarbons[1,3]	**N/A**						
C9-C10 Aromatic Hydrocarbons	**N/A**						

[1]Hydrocarbon Range data from total ion chromatogram excluding any internal/tuning standards eluting in that range
[2] C_5-C_8 Aliphatic Hydrocarbons exclude the concentration of Target APH Analytes eluting in that range
[3] C_9-C_{12} Aliphatic Hydrocarbons exclude conc of Target APH Analytes eluting in that range AND conc of C_9-C_{10} Aromatic Hydrocarbons

CERTIFICATION

Were all QA/QC procedures REQUIRED by the APH Method followed? ☐ **Yes** ☐ **No - Details Attached**
Were all performance/acceptance standards for required QA/QC procedures achieved? ☐ **Yes** ☐ **No - Details Attached**
Were any significant modifications made to the APH method, as specified in Sect 11.3? ☐ **No** ☐ **Yes - Details Attached**

I attest under the pains and penalties of perjury that, based upon my inquiry of those individuals immediately responsible for obtaining the information, the material contained in this report is, to the best of my knowledge and belief, accurate and complete.

SIGNATURE: _____ **POSITION:** _____

PRINTED NAME: _____ **DATE:** _____

APPENDIX 4

RECOMMENDED STANDARD OPERATING PROCEDURE (SOP) FOR THE COLLECTION OF AIR SAMPLES

1.0. SCOPE AND APPLICATION

1.1 The purpose of this Standard Operating Procedure is to identify and describe recommended sampling and associated quality control procedures for use with the MADEP Air-Phase Petroleum Hydrocarbons (APH) method.

1.2 This SOP describes procedures for obtaining instantaneous grab air samples, subatmospheric time-integrated air samples and pressurized time-integrated air samples. These procedures have been consolidated to allow for user discretion and applicability to APH analysis.

1.3 Sampling procedures included in EPA Methods TO14A and TO15 may also be used with the APH Method. [see "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air" (EPA/625/R-96-010b) and Method IP-1A of the "Compendium of Methods for the Determination of Air Pollutants in Indoor Air"(PB90-200288]. However, the basic procedures published in these methods specify equipment not commonly used by air sampling firms and public agencies. Nonetheless, the basic quality control requirements of these methods apply to all sampling procedures and approaches, regardless of equipment used.

1.4 Although the specific procedures recommended in this SOP are not mandatory, adequate quality control measures must be instituted in all cases to ensure and document the integrity of collected samples. These measures must include, at a minimum, steps that provide assurance of the original cleanliness and non-contamination of sample containers and any hardware touching the sample, the assurance of accurate flow measurements and sample volumes and the assurance that a sample as delivered for analysis is not altered physically or chemically from when it was taken in the field.

1.5 This SOP is based upon the U.S. Environmental Protection Agency (USEPA) Region 1 Laboratory's "Standard Operating Procedure – Sampling Volatile Organic Compounds Using SUMMA Polished Stainless Steel Canisters".

2.0 GRAB CANISTER SAMPLES

2.1 Canister Grab Sampling Equipment

2.1.1 Sample Inlet Line - Chromatographic-grade stainless steel tubing.

2.1.2 Sample Canister(s)- Certified clean and leak free stainless steel SUMMA® polished or silica lined passivated air sampling canisters, typically available in 6 and 15 liter sizes.

2.1.3 Vacuum/Pressure Gauge – Configured with appropriate fitting to attach to canister to measure vacuum before and pressure (or vacuum) after the sampling event.

2.1.4 Particulate Matter Filter – 2 micrometer pore size in-line stainless steel filter to be attached to sample inlet line.

2.2 Canister Grab Sampling Procedures

2.2.1 Collect grab samples from the breathing zone(s) of potentially impacted structures, from areas were point-source emissions of volatile contaminants are suspected (e.g., basement sumps, cracks, annular spaces around utility lines), from soil gas probes, or in a manner otherwise consistent with sampling and data quality objectives.

2.2.2 Connect the Vacuum/Pressure Gauge tightly to the canister inlet and open the canister bellows valve to verify the vacuum (should be –30 inches Hg or 0 mm Hg). Close valve and remove gauge.

2.2.3 Connect the particulate filter and sample inlet in-series to the canister inlet.

2.2.4 To take a sample, open the canister valve slightly and allow ambient air to enter the canister. Leave valve open for 1 minute to allow the canister pressure to reach ambient (0 psig/760 mm Hg).

2.2.5 Verify final pressure with the gauge and close valve.

2.2.6 In a field log notebook or sampling event form, record project name, sample date, sampling location, canister serial number, initial vacuum reading, final pressure reading and sampling time.

2.2.7 Complete appropriate Chain of Custody Form to transfer for sample analysis.

2.2.8 Ensure that all ambient pressure canister samples are pressurized to at least 5 psig (1020 mm Hg) with humidified clean nitrogen or ultra zero air for analysis. The initial and final pressures associated with this procedure must be accurately measured and documented so that the dilution effect can be adequately compensated for during final concentration calculations

3.0 SUBATMOSPHERIC TIME-INTEGRATED CANISTER SAMPLES

3.1 Equipment

3.1.1 Sample Inlet Line - Chromatographic-grade stainless steel tubing.

3.1.2 Sample Canister(s)- Certified clean and leak free stainless steel SUMMA® polished or silica lined passivated air sampling canisters, typically available in 6 and 15 liter sizes.

3.1.3 Vacuum/Pressure Gauge – Configured with appropriate fitting to attach to canister to measure vacuum before and pressure (or vacuum) after the sampling event.

3.1.4 Particulate Matter Filter – 2 micrometer pore size in-line stainless steel filter to be attached to sample inlet line.

3.1.5 Flow Controller – Adjustable mechanical flow controller, fixed orifice flow controller or electronic flow controller capable of reliably controlling flowrate under vacuum (-30 inches Hg [0 mm Hg] to -5 inches Hg [633 mm Hg)]) and under flowrates between 5 and 100 cubic centimeters per minute depending on the designated event duration. Flow controlling device must be constructed of non-contaminating materials.

3.1.6 Calibrated Flow Measuring Device – Mass flowmeter or calibrated rotameter accurate in the 0 to 100 cubic centimeters per minute range. Must be constructed of non-contaminating materials, especially if used for mid-event flow verifications.

3.2 Flow Measurement

3.2.1 Average flowrate throughout the sampling event can be determined using equation 4-1

Equation 4-1.

$$F = \frac{P \times V}{T}$$

where:

F = average flowrate (cubic centimeters [cc]/minute)
P = final canister pressure in atmospheres absolute (maximum 0.83 for subatmospheric sample)
V = Canister Volume (cc); [6 Liter Canister = 6000 cc]
T = Time (minutes)

and where:

$$P = -\frac{30 \text{ in} - \text{Final Vacuum (in Hg)}}{-30 \text{ in}}$$ for subambient samples

$$P = \frac{\text{Gauge Pressure (psig)} + 14.7 \text{ psia}}{14.7 \text{ psia}}$$ for pressurized samples

$$P = \frac{\text{Final Pressure (mm Hg)}}{760 \text{ mm Hg}}$$ for either type

3.2.2 Flowrate measurements must be made before and after the sampling event (and during if necessary) to verify that the average flowrate is consistent throughout the sampling interval.

3.2.3 Target flowrates for subatmospheric time-integrated samples should be projected and set based on an initial canister vacuum of –30 inches Hg and a final vacuum of -5 inches Hg. The residual vacuum is required to provide a flow driving force until the end of the sampling event.

3.2.4 The following are target flowrates for several event times using a 6 liter canister as calculated from the formula above.

2 Hours = 41.7 cc/min
8 Hours = 10.4 cc/min
24 Hours = 3.5 cc/min

3.2.5 Adjustable mechanical flow controllers are not likely to be stable below 10 cc/minute. Fixed orifice or low range electronic mass flow controllers would perform better for this application. Fifteen (15) liter stainless steel canisters allow higher flowrates and may be preferable for longer sampling events.

3.2.6 Flow controllers should be functionally checked and calibrated with a certified flow measuring device prior to the sampling event and rechecked in the same manner after the event. Flowrates are checked before and after sampling events using non-project evacuated canisters. Periodic flowrate checks (minimally once per hour) should be made using a non-contaminating certified rotameter or mass flowmeter during the sampling event when adjustable mechanical flow controllers are used. These measurements should be recorded and the flowrate should be adjusted up to the original set point if a significant drop is observed.

3.3 Subatmospheric Time-Integrated Sampling Procedures

3.3.1 Collect time-integrated samples from the breathing zone(s) of potentially impacted structures, or in a manner otherwise consistent with sampling and data quality objectives.

3.3.2 To start the sampling event:

3.3.2.1 Properly site the canister and verify the vacuum (–30 inches Hg or 0 mm Hg) with a vacuum gauge.

3.3.2.2 Attach the flow controller device (with filter in line), open the canister bellows valve and note the start time. Start co-located canisters at the same time if possible. Immediately check the flowrate and adjust to set point, if necessary. Note the initial flowrate.

3.3.3 To complete the sampling event:

3.3.3.1 Check and note the final flowrate. Close canister bellows valve and note the final time.

3.3.3.2 Detach the flow controller and check the remaining vacuum with the gauge. Vacuum and flowrate should be observed at the end of the event. Ambient pressure (0 psig or 760 mm Hg) indicates an excessively high flowrate set point or a leak. This observation compromises the time - integrated aspect of the sample.

3.3.4 If an automatic timer (with an electronic solenoid) is employed to time the sampling event (i.e., unattended operations), all procedures above are valid. However, extra care must be taken to ensure the accuracy of the average flowrate during the event and that the event occurred during the designated time. An elapsed time recorder/indicator should be employed with such a set up.

3.3.5 All subambient pressure canister samples should be pressurized to at least 5 psig (1020 mm Hg) with humidified clean nitrogen or ultra zero air for analysis. The initial and final pressures associated with this procedure must be accurately measured and documented so that the dilution effect can be adequately compensated for during final concentration calculations.

4.0 PRESSURIZED TIME-INTEGRATED CANISTER SAMPLES

4.1 Equipment

4.1.1 Sample Inlet Line - Chromatographic-grade stainless steel tubing. All tubing connecting inlet to sample pump and sample pump to canister should be constructed of stainless steel or a similarly inert material.

4.1.2 Sample Canister- Certified clean and leak free stainless steel SUMMA® polished or silica lined passivated air sampling canisters, typically available in 6 and 15 liter sizes.

4.1.3 Vacuum/Pressure Gauge – Configured with appropriate fitting to attach to canister to measure vacuum before and pressure (or vacuum) after the sampling event.

4.1.4 Particulate Matter Filter – 2 micrometer pore size in-line stainless steel filter to be attached to sample inlet line. This filter may be integral to manufactured sampling units.

4.1.5 Flow Controller - Adjustable mechanical flow controller, fixed orifice flow controller or electronic flow controller capable of reliably controlling flowrate under vacuum (to -30 inches Hg or 0 mm Hg) and under pressure (up to 15 psig or 1520 mm Hg) at flowrates between 5 and 200 cubic centimeters per minute, depending on the designated event duration. Flow controlling device and associated plumbing must be constructed of non-contaminating materials. Commercially manufactured samplers and shop assembled samplers can be equipped with adjustable electronic mass flow controllers/flow meters which measure and control flowrates. These devices come with digital LCD/LED flowrate displays which change with adjustment.

4.1.6 Sample Pump – Non-contaminating diaphragm or metal bellows air sampling pump capable of pressurizing an air sampling canister to a minimum of 15 psig (1520 mm Hg).

4.1.7 Calibrated Flow Measuring Device – Mass flowmeter or calibrated rotameter accurate in the 0 to 200 cubic centimeters per minute range. Must be constructed of non-contaminating materials, especially if used for mid-event flow verifications. Mass flow controller/meters must be calibrated to certified flow measuring device (soap film or equivalent) in the same manner.

4.1.8 Programmable Sampler – Programmable samplers used for unattended operation should have the following equipment.

4.1.8.1 Pump Pressure Regulator/Indicator – Used (with bypass plumbing) to adjust delivery pressure from the pump. Setting should not be less than the anticipated canister pressure, based on flowrate and sampling time.

4.1.8.2 Electronic Timeclock – For programming “On” and “Off” times for the sampling event. Timeclock should direct power to the sampling pump and outlet solenoid.

4.1.8.3 Outlet Solenoid – Electronic valve which prevents leakage of air into the sample canister before the commencement of the event and leakage out after the conclusion of the event.

4.1.8.4 Elapsed Time Indicator – Verifies the time period (in minutes) that the sample was collected.

4.1.8.5 Electrical Power Supply - In contrast to the subambient sampling procedure, all pressurized canister samplers must have access to a DC or AC electric power source.

4.2 Flow Measurement

4.2.1 All flow indicating/measuring devices used to measure the flowrate associated with the use of pressurized canister samplers must be certified to a NIST traceable device such as a soap film meter or equivalent. This includes flow controlling/measuring devices integral to the sampler and external devices.

4.2.2 All pressurized canister samplers must be flushed with clean nitrogen or ultra zero air between projects and a test canister containing humidified nitrogen or ultra zero air must be analyzed to ensure that the sampler is contamination free.

4.2.3 The projected sample flowrate should be calculated on the basis of a final canister pressure of approximately 15 psig (1520 mm Hg). A minimum of 5 psig (1020 mm Hg) is typically needed for direct analysis. The following are examples of target flowrates for typical time integrated sampling periods based on 15 psig (1520 mm Hg) final pressure for a 6 liter canister.

2 Hours = 100 cc/minute
8 Hours = 25 cc/minute
24 Hours = 8.5 cc/minute

4.2.4 For commercial samplers with pump output gauges, while running the sampler to set the flow, adjust the output pressure to 5 psig greater than the anticipated final canister pressure. This will prevent the pump and canister from reaching flow/pressure equilibrium before the end of the sampling event. A pressure equilibrium between the canister and the pump would prevent any new air flow from getting into the canister.

4.3 Pressurized Canister Time-Integrated Sampling Procedures

4.3.1 Collect time-integrated samples from the breathing zone(s) of potentially impacted structures, or in a manner otherwise consistent with sampling and data quality objectives.

4.3.2 To start the sampling event, position the sampler in a location with access to power. Turn on the sampler to check pump pressure and to measure and adjust flowrate (using the certified flow measurement device). Running the sampler at this time will also purge sampler plumbing with ambient air. Note the initial flowrate on field sheet and/or notebook.

4.3.3 Turn off the sampler and connect the evacuated canister. Take an initial vacuum reading with a gauge prior to connecting or note reading on integral sampler gauge to make sure canister vacuum is at –30 inches Hg.

4.3.4 Open canister bellows valve and start sampler at the designated start time. Note start time on the field sheet or notebook.

4.3.5 Periodically check sampler to make sure that it is operating correctly. If sampler has an integral vacuum/pressure gauge, check pressure to verify that the current reading is consistent with the flowrate and the elapsed time.

4.3.6 At the end of the sampling interval, close the canister and detach from the sampler. Take a final flowrate measurement and note it on the field sheet. Note the final time on the field sheet or notebook.

4.3.7 Check the final pressure on the canister sample and note on field sheet or notebook. Note whether final pressure equaled the projected final pressure.

4.3.8 For programmed sampling intervals, check initial flows and pressures as discussed above (turn on sampler manually). Follow manufacturer procedures for programming time clock. Delete any inappropriate timer programs from the clock's memory and recheck the current sampling interval program to make sure that sampler will turn on and off at the correct designated times (and correct day).

4.3.9 Reset Elapsed Time Indicator and make sure time clock is in the "Automatic " mode for timed events (not manual "On" or "Off").

4.3.10 After completion of the timed event, close bellows valve on the canister and detach. Check pressure on canister and note on field sheet or notebook. Verify that the final pressure is approximately at the original projected final pressure. A low or zero final pressure indicates that the canister leaked after sampling or that the flowrate dropped during the event.

4.3.11 Note the elapsed time and verify that it is equal to the programmed sampling interval.

4.3.12 Manually turn on sampler and check final flowrate and pump pressure. Note final flowrate on the field sheet or notebook.

5.0 ADDITIONAL QUALITY CONTROL PROCEDURES

5.1 Specifications in EPA Method TO14A describe a "clean" canister as having a pressure of 0.05 mm Hg or about 50 millitorrs. Practically, the pressure could be 2 or 3 times the 50 millitorr value if the contamination standard is met.

5.2 One evacuated canister per sampling event should be submitted for analysis as a field blank. This canister should be filled to a minimum of 10 psig (1267 mm Hg) with humidified ultra zero air or clean nitrogen used to dilute underpressurized field samples.

5.3 Side by side duplicate samples should be taken at least one location per each sampling event for precision. Preferably, they should sample at a location where moderately high (but not excessively high) concentrations of analytes of concern could potentially be found.

5.4 Care should be taken to separate each sampling zone while sampling is occurring (e.g., keep doors between floors shut).

5.5 Carefully note conditions under which the sample is taken which might affect the interpretation of the results including unusual weather conditions, air temperature, current building ventilation status and the presence of petroleum related products on site.

6.0 SAMPLE CATEGORIES AND NOMENCLATURE

6.1 Below are definitions of sample location zone categories which should be used to help identify and codify the type, source, and relevance of reported APH data.

6.1.1 **Zone A** – Samples are obtained at vapor entry points into a building (e.g., breach in foundation, sump hole). Samples are used to identify areas of point-source vapor emissions into impacted structures and/or for investigative/health screening purposes. Typically, an instantaneous grab samples, though sample volume may need to be metered to avoid overwhelming the analytical system.

6.1.2 **Zone A-1** – Soil gas samples. Samples are obtained from temporary or permanent subsurface probes. Typically an instantaneous grab sample, though sample volume may need to be metered to avoid overwhelming the analytical system. Care must be exercised to avoid short-circuiting the sample pathway by the use of a high sampling vacuum or flowrate. Care must also be exercised to avoid or prevent entrapment of groundwater.

6.1.3 **Zone B** – Samples taken in unoccupied (and unfinished) areas on building levels in contact with the soil. Little personal exposure is expected. This sample could be an instantaneous grab or time integrated sample

6.1.4 **Zone C** – Samples taken in occupied, finished part of the building level in contact with the soil. Some personal exposure could be expected, depending on the extent of the area's use. This should be a time-integrated sample.

6.1.5 **Zone D** – First floor living area. Personal exposure level depends on percentage of time occupied and whether sleeping quarters are located on this level. Time-integrated samples are appropriate.

6.1.6 **Zone E** – Second or higher floors. Occupied during sleeping or other hours. This zone needs to be considered if there is a major contamination situation, there is a direct air connection with the level of entry or if it is occupied by an unusually sensitive receptor. Time-integrated samples are appropriate.

6.1.7 **Outside/Ambient** – Used to assess the influence and impacts of outdoor air quality on indoor air quality. Also can be used as an additional quality control sample because background ambient air concentrations of volatile petroleum hydrocarbons are at well documented average levels at most locations. Time-integrated samples are appropriate.

7.0 REFERENCES

Standard Operating Procedure Sampling Volatile Organic Compounds Using SUMMA® Polished Stainless Steel Canisters, EPA-REG1-ESD/CAN-SAM-SOP, March 1994. US Environmental Protection Agency, New England Regional Laboratory, Environmental Services Division, 60 Westview Street, Lexington, MA 02173.